EEE BRANCH REVIEW

DATE: IN _____ OUT _____ 12/ IN 22/76 OUT 8/23/77 IN _____ OUT _____

FISH & WILDLIFE (ENVIRONMENTAL CHEMISTRY) EFFICACY

FILE OR REG. NO. 39365-R

PETITION OR EXP. PERMIT NO. _____

DATE DIV. RECEIVED _____

DATE OF SUBMISSION _____

DATE SUBMISSION ACCEPTED 3CID-2B-Yes

TYPE PRODUCT(S): I, D, H,(F) N, R, S _____

PRODUCT MGR. NO. J. Lee (22)

PRODUCT NAME(S) Everseal

COMPANY NAME Everseal Manufacturing Company

SUBMISSION PURPOSE Use as a Preservative for Canvass

CHEMICAL & FORMULATION Copper 8-Quinolinolate

1.0 Introduction

1.1 Everseal's application (Form 8570-10) indicates the product (39365-R) is for use only by governmental agencies. The label states "Preservative coating, canvas, (which meets) FED. SPEC. TT-P-5952, TYPE-I, CLASS-I, Mildew... Resistant...(paste)."

1.2 The data package consists of one volume ACC No. 025539 (3/31/74).

1.2.1 References which related to environmental chemistry:

A. Detection of Cunilate 2174 - No (Copper 8-quinolinolate) in Milk/Adhesives - Syracuse University - CAR Item

B. Analytical report on migration of metals in Cunilate into various fruits and vegetables - 1959

C. Letters and Test data on migration of Cunilate to Tomatoes - Industrial Bio-test Laboratories, Inc. - 1960

D. An Analytical Method for determining Copper 8-quinolinolate (Solubilized) in Treated Wood - Scientific Chemicals, Inc.

2.0 Direction for Use

2.1 Application rate as a preservative coating for canvas:

"Mix with an equal volume of a petroleum solvent. Approximately one gallon of the diluted preservative coating is sufficient to cover 10 square yards of fabric surface. Apply to dry fabric. Allow to dry thoroughly before folding or storing."

2.2 Environmental Hazards:

This product is toxic to fish. Treated effluent should not be discharged where it will drain into lakes, streams, ponds or public water. Do not contaminate water by cleaning of equipment or disposal of wastes. Apply this product only as specified on this label.

2.3 Storage and Disposal:

Prohibitions: Do not contaminate water, food or feed by storage or disposal. Open dumping is prohibited.

Pesticide Disposal: Product that cannot be used or chemically reprocessed should be disposed of according to procedures approved by Federal, State or local disposal authorities.

Container Disposal: Triple rinse (or equivalent) and offer for recycling, reconditioning, or disposal in approved landfill or bury in a safe place.

General: Consult Federal, State or local disposal authorities for approved alternate procedures.

3.0 Discussion of Data

3.0.1 The use-directions do not specify the canvas materials treated, but "FED SPEC TT-P-5952" indicates the product is suitable for tents and tarpulins.

3.0.2 Studies (ancillary) are referenced which relate to the "migration" of the a.i. from materials other than canvas.

(1) "Detection of Cunilate 2174- No [Copper-8-quinolinolate] in Milk Carton Adhesives" Lundgren, D. and Reed, E. Syracuse University.

Pint cardboard cartons were assembled with an adhesive (0.5 gm/carton) containing Cunilate (0.3%); 1.5 mg. of the a.i. per carton. Leaching tests [2, 5 and 7-days/8° and 28°C/One shake/8-hours] indicated copper concentrations in the leach water (distilled) of both control and test leachates of CA 0.002-0.004ppm. The reported figures approximate the sensitivity of the method (0.002ppm).

Conclusion: If the a.i. leached the amount leaching, based on copper in the leachate, was less than the sensitivity of the procedure.

(2) "Analytical Reports on migration of metals in Cunilate into various fruits and vegetables - 1959;" Spectro-chemical Res. Lab's Inc., Chicago 25, Ill.

Laboratory Reports (5/1/59) from the Spectro-chemical Research Labs., Inc. Chicago, Illinois, indicate no difference between the copper (Ni also Mn) content of several (9) vegetables and fruit samples [presumably in contact with treated wood surfaces] and control samples. Details of the testing are not reported. "Scientif Oil Compounding Co." refers to these tests in their letter (2/22/60) to IBT.

Conclusion: The study does not contain useful information.

(3) Letters and test data on migration of Cunilate to tomatoes - Industrial Bio-test Laboratories, Inc. - 1960 - Data was generated by Scientific Oil Compounding Co., Inc.

Wooden panels from tomato lug boxes treated (2.5% Cunilate dip) as recommended, were leached for 72-hours (dip) with either dilute acetic acid (1%) or tomato juice. Copper residues found in the juice-leachate (CA 0.2ppm) may be due to inorganic impurties in the product; this leachate was not analyzed for the organic moiety of the a.i. However, the acetic acid leachate was analyzed for the a.i. on the basis of the organic moiety and the amount of a.i. leaching was below the detectable limits (0.001 mg/Liter) of the procedure.

Conclusion: If the a.i. was leached by either tomato juice or dilute acetic acid the amount leaching was less than the sensitivity of the procedures.

(4) "An Analytical Method for Determining Copper-8-Quinolinolate (solubilized) in Treated Wood;" Chowdhry, R.M. Scientific Chemicals, Inc., Chicago, Ill.

[redacted]

Conclusion: Although raw analytical data is not presented the method appears scientifically feasible, but only for determining (0.5ml titer) a.i. concentrations in leach exceeding 200ppm.

5.0 Recommendations

Note to P.M.:

(1) The incremental risks associated with the proposed use would be small, refer to memos from Mr. E. L. Johnson (5/12/77) and D. D. Campt (5/13/77), since copper-8-quinolinolate is currently used in Cunilates as a fungi-static additive to paper, oil, wood, and other materials. The dosage rate of the proposed and accepted products are not significantly different.

(2) There are no formal environmental chemistry requirements for preservatives applied to canvas materials.

(3) There is data generated by Scientific Oil Compounding Co., Inc., and sent to IBT. We do not know what IBT has to do with the data. The data was not used for this submission.

5.1 We cannot concur with the proposed use.

5.2 The procedure for the disposal of excess wastes is not clear. Where will such wastes be discharged?

(a) If the discharge is into wastewater treatment systems we will need the aquatic impact studies in the Indirect-Discharge column of the attached sheet.

(b) If the precaution against discharge into "... ponds or public water" is deleted; or if the fungicide pass through the wastewater treatment facility, we will need the aquatic impact studies in the Direct-Discharge column of the attached sheet.

5.3 Examples of acceptable protocols for environmental chemistry studies follow:

Hydrolysis:

Hydrolysis data are required for all pesticides. Studies are conducted in darkness using radioisotopic or other comparable techniques at different pH values (acidic, neutral and basic) at two concentrations and two temperatures. Aliquots in duplicate should be taken at four sampling time intervals, with at least one observation made after one-half of the pesticide is hydrolyzed, or thirty days, whichever is shorter. A material balance (the total accountability at the completion of an experiment of the pesticide introduced into a defined system including both identified and unidentified products) half-life estimate, and identification of degradation products for the pesticide must be provided. Studies utilizing distilled water provide an upper limit estimate for persistence of pesticides in the aquatic environment. Hydrolysis in natural waters may be carried out to supplement studies in distilled water.

Activated Sludge Metabolism:

Pesticides discharged into wastewater treatment systems may be transformed or disrupt the treatment process. A study of effects of pesticides on the wastewater treatment process is required. Synthetic sewage (nutrients) and radioisotope material are added to activated sludge and aerated in a closed system for 23 hours; the sludge is allowed to settle for 30 minutes. A liter of supernatant (effluent) is removed for pesticide residue analysis including a material balance. Fresh synthetic sewage and test compound are added to the remaining sludge and the cycle including fresh synthetic sewage and test compound, is repeated. Dosage should start at 0.1 ppm and increase by increments to 100 ppm. Effects on microbial population must be determined by daily total counts of viable organisms in sludge.

Photolysis:

Photodegradation studies in water are required for all uses. Studies in soil are required for crop uses. Conduct photodegradation studies using radioisotopic or comparable techniques at one concentration under natural or simulated (greater than 280 nm 280 x 10^{-9} meters wavelength) sunlight. Such studies must provide material balance half-life estimate and the identification of photoproducts. Rate studies are conducted in distilled or deionized water and sampling should continue until twenty percent degradation is observed, and for thirty days to identify photoproducts. Yield of photoproducts may be increased by changing such conditions as wavelengths, concentration, photosensitizers and solvents other than water. Supplemental rate and photoproduct studies may be carried out in natural water for aquatic uses. Studies performed on the soil used in the soil metabolism studies are preferred but other soil textures will be acceptable. The intensity of incident sunlight and time of exposure must be reported if sunlight is used as a source.

Photodegradation data must be supported by incident light intensity and percent transmission. Values for intensity in candles and lambert units are required for artificial light sources. Latitude, time of year, atmospheric cover, and other major variables which affect incident light are to be reported when natural sunlight is used.

Aerobic Aquatic Metabolism:

The study is required for all aquatic uses and aquatic impact uses which result in direct discharges into the aquatic environment. Metabolism of radiolabeled chemicals equivalent to the anticipated rate of application or discharge is studied in water representative of that found at or near the intended use sites.

These studies are to continue until decline curves have been established or to thirty days.

Anaerobic Aquatic Metabolism:

An anaerobic study assesses the availability of pesticide residues to irrigated crops, to areas where water is recycled for production of aquatic crops and to other parts of the aquatic food web. Rate, type and degree of metabolism of the pesticide are determined in water plus sediment taken from an impoundment like that found at or near proposed use sites. The preferred substrate for this study is sediment, but the use of flooded soils may be adequate. Oxygen depletion is established by flooding for thirty days prior to dosing at the approximate field rate. Data are collected until a ninety percent loss of pesticide occurs and until patterns of formation and decline of metabolites are established in water and sediment. Studies are conducted using radioisotopic or other comparable techniques.

Adsorption/Desorption:

Adsorption of pesticides to soil, sediment and particulate matter mitigates the availability and concentration of pesticides in water as well as leaching and volatility of pesticides. A laboratory study using radioisotopic or comparable techniques is required.

Adsorption coefficient is determined using one soil and four concentrations in distilled water. Additional sediments will be required if the sediment characteristics vary sidely among proposed use sites. Desorption coefficient is determined on the same sediment.

Water Dispersal:

Pesticides dispersed throughout the aquatic environment from aquatic uses and aquatic impact uses, if discharged into aquatic sites, represent a hazard throughout the aquatic environment. Due to variability of aquatic environment, a field study tailored to one or more representative sites establishes the concentration in water at selected distances from sites of exposure. Analysis of pesticide residues in water using chemical or comparable bioassay procedure is required. Analysis or residue buildup in selected indicator organisms using chemical methods is required.

Effects of Microbes on Pesticides:

Impact of microbes on pesticide transformation include comparisons of metabolic processes under sterile and non-sterile conditions during a thirty-day period. Preferred sampling intervals are 1, 3, 7, 14 and 20 and 30 days, but other intervals may be appropriate.

Acceptable soil sterilization methods are heat or high energy ionizing radiation. Attempts should be made to identify organisms responsible for degradation. For organisms which are difficult to identify, family names will be sufficient. Isolates that cannot be identified to family level must have descriptive characteristics which can be substituted for generic classification. Alternately, studies utilizing pure or defined and characterized mixed cultures of bacteria, algae and/or fungi are adequate.

Effects of Pesticides on Microbes:

Data on Effects of pesticides on microbes are obtained from studies of effects on microbial functions or microbial populations. Studies of effects on microbial function constitute a more direct approach, and are preferred to studies of effects on populations. Some effects cannot be measured directly and population studies may be the only recourse. When the functional approach is chosen, the effects on nitrogen fixation, nitrification, cellulose, starch and protein degradation are required. When the population approach is chosen, effects on pure or mixed culture populations of representative microorganisms from soil or water or obtained from culture collections are required. Appropriate organisms include free-living nitrogen-fixing bacteria and blue-green algae such as Azotobacter, Colostridium, Cytophaga, Streptomyces, Penni-cillium, Flavobacterium, Trichoderma, Aspergillus, Chaeto-mium, and Fusarium.

Animal or plant pathogens and indicators of fecal pollution are unsuitable.

Information on organism identity and media must be supplied. Organisms used as indicators must be identified by Linnaean name as well as common name. Cultures of micro-organisms obtained from collections must also be identified

by collection code numbers; other sources of microorganisms must be described. Photographic evidence for claimed pure cultures not derived from collections must be submitted. Standard maintenance and test media must be identified and other media identified and described.

Fish Accumulation:

Accumulation of residues in nontarget aquatic organisms is an indication of contamination of the food web.

Radioisotopic or comparable techniques are employed. Two exposure systems are required: Flow-through (with constant concentration of aqueous solution of pesticide) and static (with ambient concentration of residues from treated soil). Bluegill sunfish are preferred in flow-through and catfish are required in the static system.

For the static system, sandy loam soil is treated at use rate and aged under aerobic conditions for two to four weeks prior to initiation of fish exposure. Exposure duration is 30 days with sampling at 0, 1, 3, 7, 10, 14, 22, and 30 days of exposures.

Fish and water samples are taken on 0, 1, 3, 7, 10 and 14 days of depuration. Soil and water samples are also obtained prior to fish exposure interval. The amount and identity of the residue is determined for water, soil, whole body fish, edible tissue and viscera or carcass at each sample interval.

R.W. Cook Acting 9-19-77

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